FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation under USAF Contract AF 33 (616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials," Task No. 735002 "Refractory Inorganic Non-Metallic Materials: Graphitic"; Project No. 7381 "Materials Application, "Task No. 738102 "Materials Process"; and Project No. 7-817 "Process Development for Graphite Materials." The work was administrated under the direction of the AF Materials Laboratory, Deputy Commander/Research and Engineering, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted at the Research Laboratory of the National Carbon Company located at Parma 30, Ohio, under the direction of J. C. Bowman, Director of Research and W. P. Eatherly, Assistant Director of Research.

It is a pleasure to acknowledge the work of V. W. Kessler in machining the samples. The help of M. L. Alley and G. M. Svach in the operation of the camera contributed greatly to the success of this work. J. T. Meers provided the pyrolytic graphite specimens.

Other reports issued under USAF Contract AF 33(616)-6915 have included:

WADD Technical Notes 61-18 and 61-18, Part II, progress reports covering work from the start of the Contract on May 1, 1960 to October 15, 1961, and the following volumes of WADD Technical Report 61-72 covering various subject phases of the work:

Volume I	Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
Volume II	Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
Volume III	Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.
Volume IV	Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.
Volume V	Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.
Volume VI	Creep of Carbons and Graphite in Flexure at High Temperature, by E. J. Seldin.
Volume VII	High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar and K. J. Zeitsch.

ABSTRACT

The thermal expansions of lampblack base, coke base, hot worked coke base and pyrolytic graphites have been measured in the c_o direction from 1000° to 2700°K by use of a high temperature X-ray camera. The results indicate that, (a) the coefficient of thermal expansion is not constant with temperature and (b) this coefficient increases with increasing crystallite perfection. The camera was modified to accept a low temperature attachment and the a_o's and c_o's of lampblack base, hot worked coke base, and pyrolytic graphite were evaluated at 6°, 78° and 298°K. The three graphites showed similar expansion characteristics and, within the limits of error, seemed to show a negative a_o expansion coefficient near 298°K.

This technical documentary report has been reviewed and is approved.

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1. INTRODUCTION

X-ray diffraction offers the only technique for determining the thermal expansion of polycrystalline solids in specific crystallographic directions. Dilatometric techniques can measure an average expansion but gather little information about possible anisotropies in the crystal[1,2]. The need for more precise information about thermal expansion in graphite is created by graphite's highly anisotropic properties and by the influence of microstructure, preferred orientation, and binder on the thermal behavior of the bulk material. A high temperature X-ray camera is ideally suited for such an examination and has been used in the temperature range of 300 to 1000°K by a number of investigators[3,4,5,6]. In this work, a high temperature camera was used in which samples could be studied at temperatures greater than 2500°K. To obtain a more complete picture of the expansion behavior, an attachment was made for the above camera to extend its working range to low temperatures, i.e., 6°K.

In addition, another variable was introduced into the investigations: the degree of crystallite perfection. Since artificial graphites exhibit widely varying degrees of crystallite perfection, no work on graphite is complete without an understanding of the effect of this variable. Therefore, a selection of samples was made which would be representative of the types of graphites normally encountered.

2. EXPERIMENTAL PROCEDURE

2.1. Samples and Preparation

Four different graphites were chosen to include variations in raw materials and representative methods of forming: (1) Grade CEP, a lampblack-base material of poor crystallinity and almost random orientation; (2) Grade TSX, a petroleum coke-base graphite of somewhat better degree of crystallinity and more orientation; (3) Grade ZTA, another petroleum coke-base material with a still greater degree of crystallinity and orientation, and (4) a pyrolytic graphite deposited at 2400°K and rebaked at 3400°K to obtain nearly perfect crystallinity and one of the highest degrees of orientation obtainable in manufactured graphite. The first three materials were formed into specimens for the high temperature camera by machining blocks of materials into 0.025 inch diameter rods one inch in length. The pyrolytic samples had been deposited in the form of rods 0.025 inch in diameter and six inches long, and were simply cut to the desired length.

2.2. Loading

The high temperature samples were inserted into tapered graphite collets and in turn pushed securely into the copper electrodes as shown in Figures 1 and 2. This assembly was placed in the camera and the system was evacuated to a pressure of 1.0×10^{-7} mm Hg. Since it was found that the use of one atmosphere pressure of nitrogen, argon or helium did not significantly retard vaporization of the sample, all runs were made in vacuo as a precaution against sample contamination.

The low temperature samples were mounted in the end of the low temperature attachment (see Figure 3). Evacuation of the camera and the insulating walls of the Dewar was accomplished by the same vacuum pumps. The working pressure at low temperatures was 5.0×10^{-8} mm Hg.

2.3. Heating and Control

The samples were self-heated by passing current through them; an input power of seventy-five watts was usually enough to achieve maximum temperature. The upper limit of temperature obtainable was determined by the evaporation rate of the carbon. Failure usually occurred as a result of the development of a hot spot, which further increased vaporization and resulted in a localized failure. This took place at approximately 2800°K for most samples. Sample temperatures were read with a Pyro Micro-Optical Pyrometer, which had been calibrated through the sight window. Temperatures were corrected for emissivity by using a value of 0.9. The control of the sample temperature was accomplished by regulation of the input voltage with a resulting variation during exposure of generally ± 10°K.

2.4. Cooling

Temperatures with the low temperature attachment were 6°, 78° and 193°K and were obtained by filling the Dewar with liquid helium, liquid nitrogen, and

FILM POSITIONING PIN

MICROFOCUS X-RAY SOURCE

HEATER LEADS

VAC ION PUMP

TO PYROMETER

PYROMETER PORT SHUTTER MANIPULATOR

TO POWER SUPPLY FOR PUMPS AND CAMERA

VAC ION PUMP

FORELINE TO VACUUM PUMP

HIGH VACUUM ISOLATION VALVE

PRESSURE GAUGE

ZEOLITE FORELINE TRAP

GAS MANIFOLD

METHANE

NITROGEN

ARGON

HELIUM

N-1315
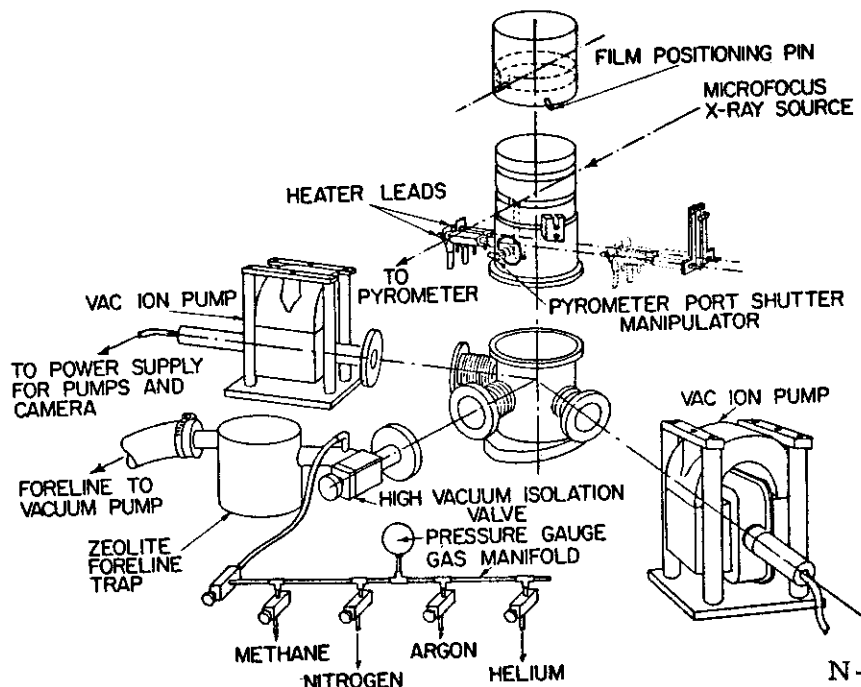
Figure 1. Exploded View of High Temperature Debye Camera

GRAPHITE COLLETS

SAMPLE
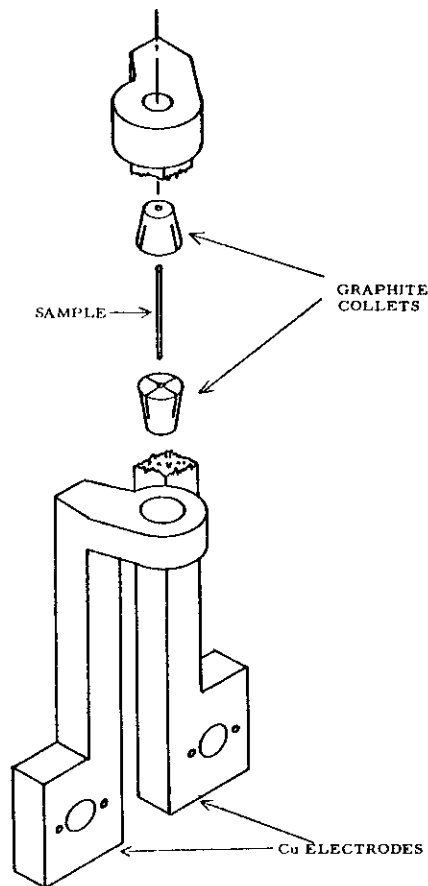
Cu ELECTRODES

N-2080

Figure 2. Assembly for Direct Heating of Conductors

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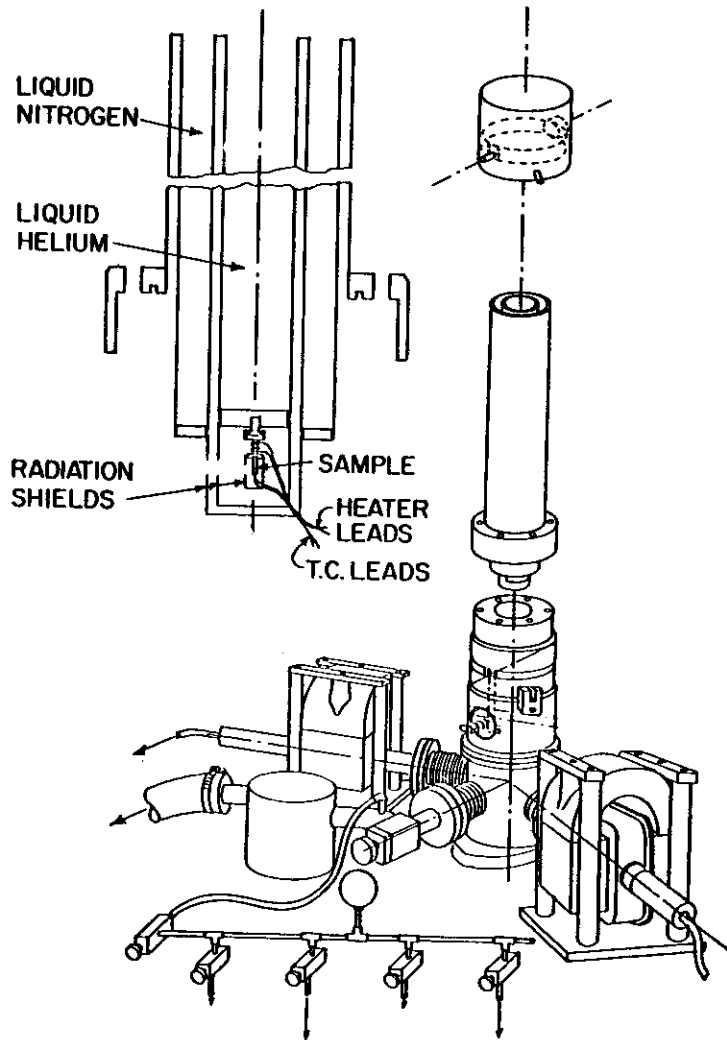
N-2291

Figure 3. Exploded View of Low Temperature Attachment

dry ice-acetone, respectively. Sample temperatures were measured with a 0.003 inch diameter differential thermocouple of chromel-constantan by placing one junction in the bath and the other on the sample.

2.5. Exposure Conditions

The use of a Jarrell-Ash Micro Focus X-Ray unit allowed a reduction of the usual two to four hour exposure time, an advantage with high temperature diffraction work. A copper target was used at 50 KV and 2 MA; the focal spot was 40 x 120 μ and was viewed from one end with a six degree take off angle. Under these conditions the typical exposure time was ten minutes for the high temperature samples and twenty minutes for those at low temperatures*.

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*The increase in exposure time at low temperatures allowed a clearer pattern in a temperature range in which speed was not important.

2.6. Measurement

Although Straumanis film loading was used, normal techniques could not be used for determining the effective camera diameter since graphite, except in the cases of natural flake or the best pyrolytic, yields poor or no back reflection lines on a Debye pattern. Four fiducial marks, ninety degrees apart along the circumference, were transferred from the film holder to each film. All the lines and fiducial marks of films were measured to 0.1 mm on a General Electric viewer and measuring device.

2.7. Evaluation

Lattice constants were evaluated from the highest order available on all films; these constants were usually obtained from the (004) for c_0 and (110) for a_0. The accuracy of these measurements is $\pm$ 0.1 per cent. Since the total expansion in a_0 is of the order of 0.1 per cent in the temperature range of from 290° to 2800°K, no evaluation of the a_0 expansion coefficient could be made; however, c_0 was plotted as a function of temperature for all samples and the related expansion coefficient was determined by graphical measurements of the slope of the curve at various temperatures. The low temperature data are based on five runs at each temperature with the film of each run measured ten times. At the low temperatures, higher orders of reflections, (008) and (510) were present on the films obtained with the pyrolytic sample.

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3. RESULTS

A typical series of films of Debye patterns for grade ZTA graphite are shown in Figure 4. These patterns demonstrate the lack of available orders of reflections required for precise lattice constant determination. The spots in the upper half of each film are the ninety degree fiducial marks discussed above. The plots of c_0 versus temperature are shown in Figures 5, 6, 7 and 8. The variation of the coefficients of thermal expansion with temperature are shown in Figure 9. The coefficients for grade TSX, which are only slightly lower than those for grade ZTA, have been omitted for clarity. The major point of interest is that there is a significant difference of the temperature dependence of the thermal expansion coefficients among the grades of graphite evaluated. In brief, as the degree of crystallite orientation and perfection increases, the thermal expansion coefficients increase.
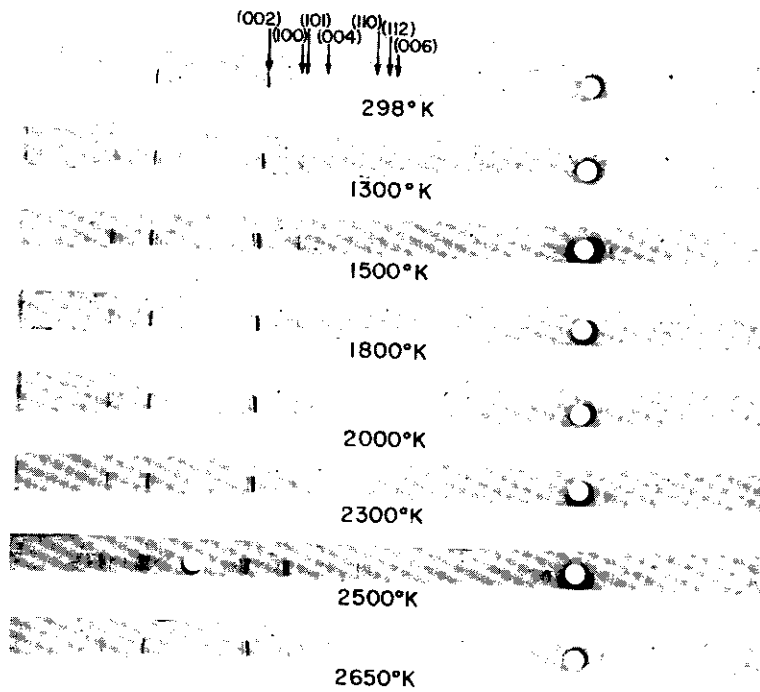
Figure 4. Debye Patterns of ZT Graphite at Elevated Temperatures

N-2238

In contrast, the low temperature thermal expansion behavior, as summarized in Table 1, does not differ greatly from grade to grade. The pyrolytic and grade ZTA graphites, whose patterns were of sufficiently high quality to allow greater precision, showed a negative a_0 thermal expansion coefficient between 78° and 298°K.
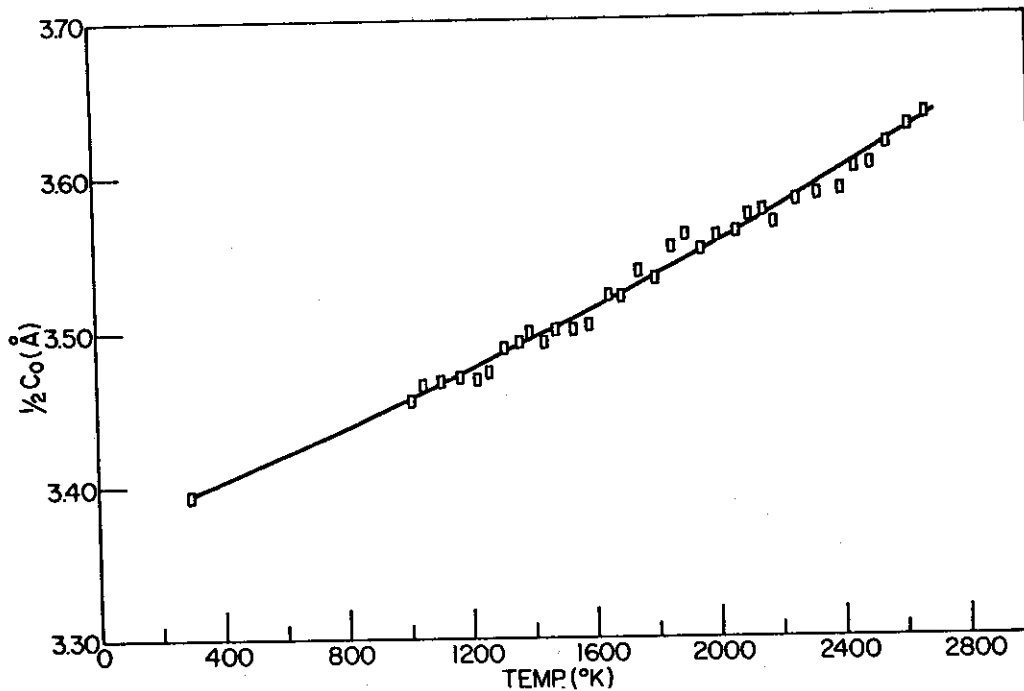
Figure 5.   Thermal Expansion of Grade CEP Graphite

N-1744
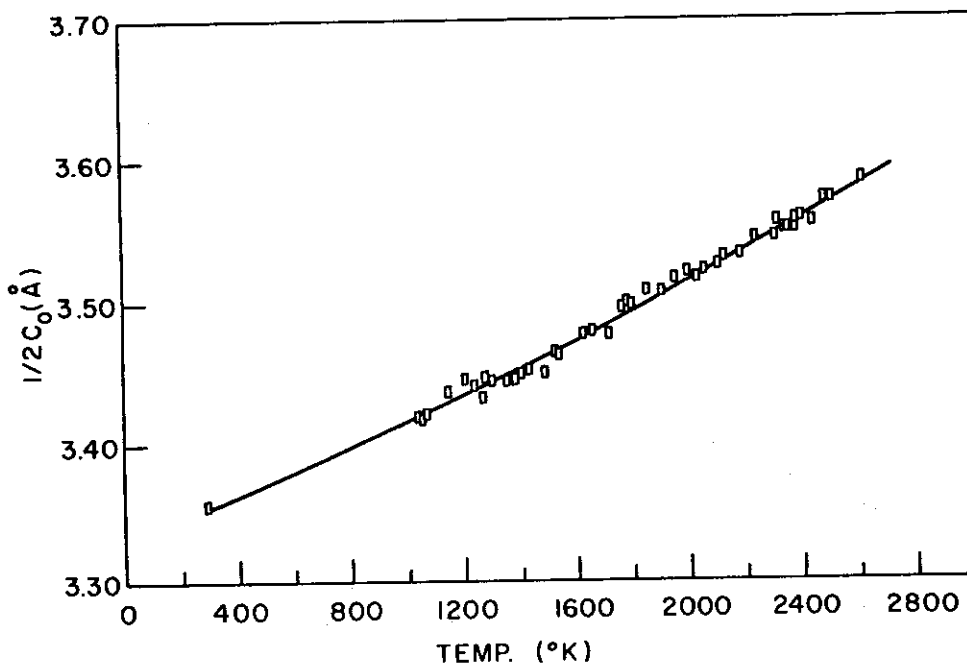
Figure 6.   Thermal Expansion of Grade TSX Graphite

N-2173

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Figure 7. Thermal Expansion of Grade ZTA Graphite

N-1743
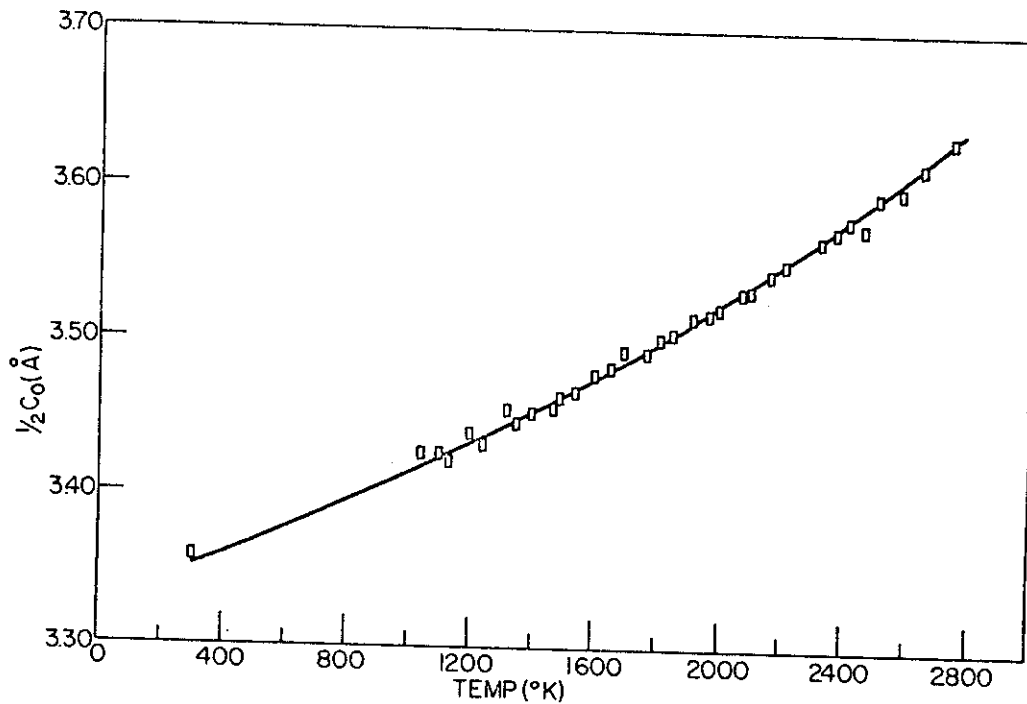
Figure 8. Thermal Expansion of Pyrolytic Graphite

N-1742

$$\alpha_c = \frac{1}{(C_0/2)_T}\left[\frac{d(c_0/2)}{dT}\right]$$

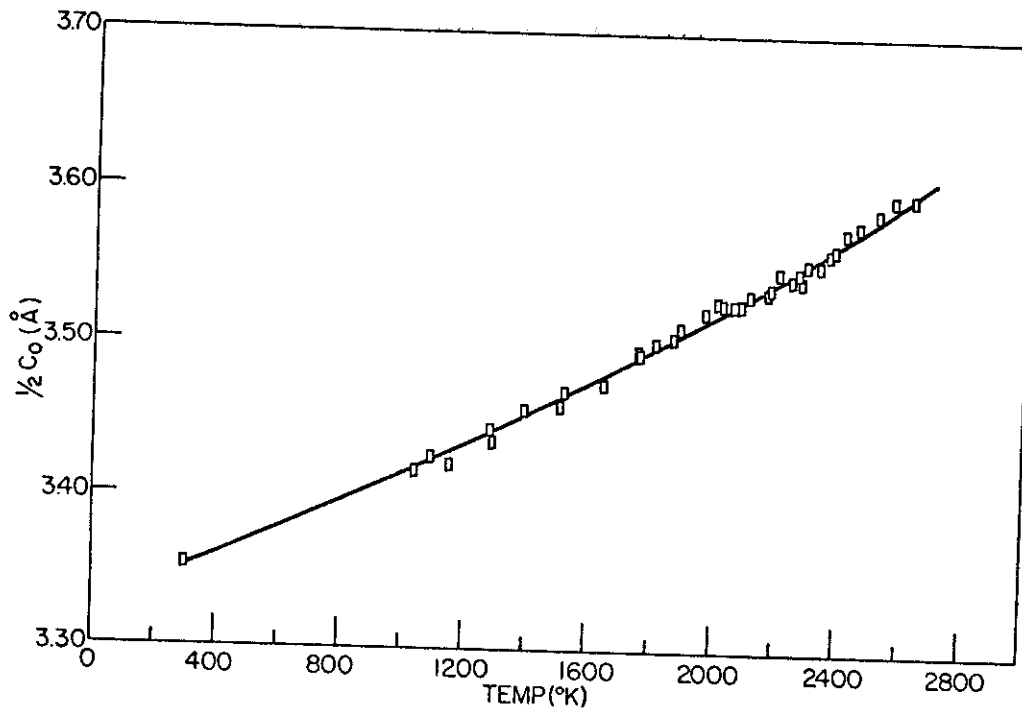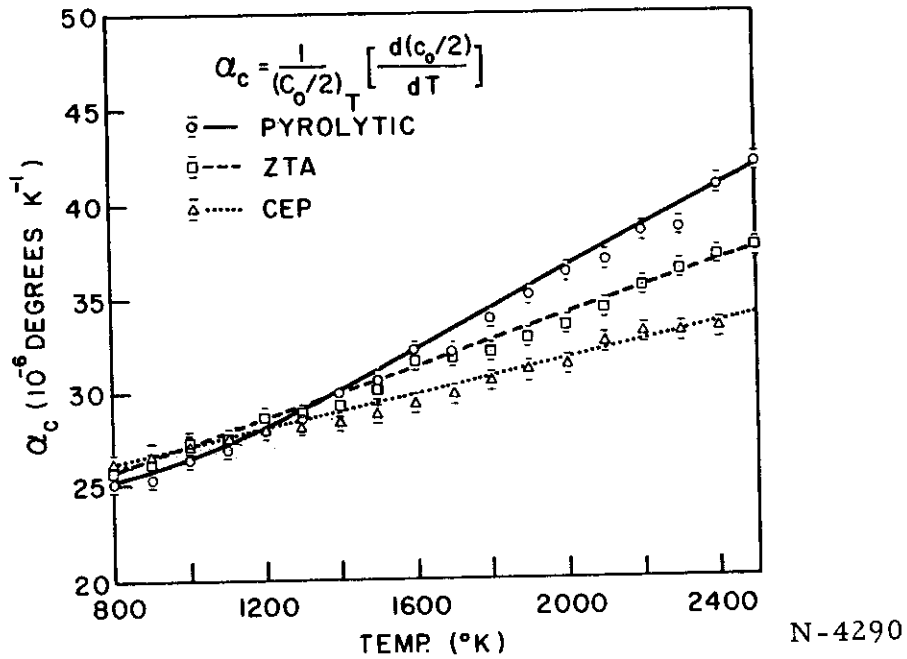Figure 9. Linear Coefficient of Thermal Expansion of Graphites

Table 1. The Lattice Constants of Graphites at Low Temperatures

Material	T (°K)	1/2 c_O (Å)	a_O (Å)
Pyrolytic	6	3.3371 ± 0.0005	2.4619 ± 0.0002
	78	3.3382 ± 0.0005	2.4623 ± 0.0002
	193	3.3467 ± 0.0005	2.4617 ± 0.0002
	298	3.3549 ± 0.0005	2.4612 ± 0.0002
Grade ZTA	6	3.345 ± 0.001	2.4616 ± 0.0005
	78	3.346 ± 0.001	2.4619 ± 0.0005
	193	3.353 ± 0.001	2.4596 ± 0.0005
	298	3.363 ± 0.001	2.4591 ± 0.0005
Grade CEP	6	3.384 ± 0.002	2.459 ± 0.001
	78	3.386 ± 0.002	2.458 ± 0.001
	193	3.392 ± 0.002	2.459 ± 0.001
	298	3.403 ± 0.002	2.457 ± 0.001

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4. DISCUSSION

Two explanations have been proposed for the observed differences in high temperature thermal expansion among the various grades of graphite. The first suggests that crystallites within a particle of graphite would restrain the c_0 expansion of each other by their mutual misorientation. In this view, one crystallite would tend to pin its neighbors and prevent them from reaching their full expansion. This effect would be strongly dependent upon the degree of orientation: the less random the arrangement of the crystallites, the less restraint upon expansion, as the major proportion of expansion would be along much the same direction for the majority of the crystallites. The thermal expansion behavior determined in this work does seem to follow this trend, if one assumes that the bulk orientation is a good measure of the orientation within the particles. A note of caution must be added; the assumption is made in the above that the forces required to subdue the true expansion are less than those which would cause creep and resulting relaxation of the restraint. This has not been shown to be the case.

The alternative explanation postulates the presence of carbon atoms lying between the layer planes and forming cross links of greater strength than the normal interlayer bonding. Such interstitial carbon atoms might have two effects: (1) A larger room temperature c_0, and (2) A restraint on any tendency to expand due to thermal agitation. This picture also fits the observed data inasmuch as the rate of thermal expansion increases with decreasing room temperature value of c_0. While the author leans toward the second explanation, more work must be done on crystallite orientation within a particle and on other aspects of the problem before an intelligent choice can be made.

Below room temperature the thermal expansion behavior seems to be nearly the same for the graphites investigated. Just how similar the expansions are is not clear, as the errors in the measurements are very close to the total changes involved, particularly expansion in a_0. The present work confirms the findings of Baskin and Meyer [7] in that a negative coefficient of thermal expansions of a_0 was found between 77° and 298°K. This negative coefficient is apparent in the pyrolytic graphite and grade ZTA, but is masked, if present at all, in the grade CEP graphite.

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5. <u>CONCLUSIONS</u>

1. The rate and total amount of thermal expansion is about one hundred times greater in the c_0 than in the a_0 dimension for SA-25, TSX, ZTA and pyrolytic graphites between 298° and 2800°K.

2. The rate of thermal expansion decreased with decreasing crystallinity in this temperature range.

3. The decrease in rate of thermal expansion is thought to be due to an increase in cross linking between the layers.

4. The c_0 thermal expansion is essentially the same for varying degrees of crystallite perfection between 6° and 298°K.

5. The a_0 thermal expansion coefficient is negative between 77°K and 298°K for Pyrolytic and ZTA Graphites.

6. <u>REFERENCES</u>

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